2nd International Electronic Conference on Water Sciences (ECWS-2)

16–30 November 2017
Chaired by Prof. Dr. Maria Filomena Camões & Prof. Dr. Kevin B. Strychar

Sponsored by: MDPI water

Decomposition of Contaminants of Emerging Concern in Advanced Oxidation Processes

Dr. Edyta Kudlek

Faculty of Energy and Environmental Engineering, Konarskiego 18, 44-100 Gliwice, Poland
edyta.kudlek@polsl.pl

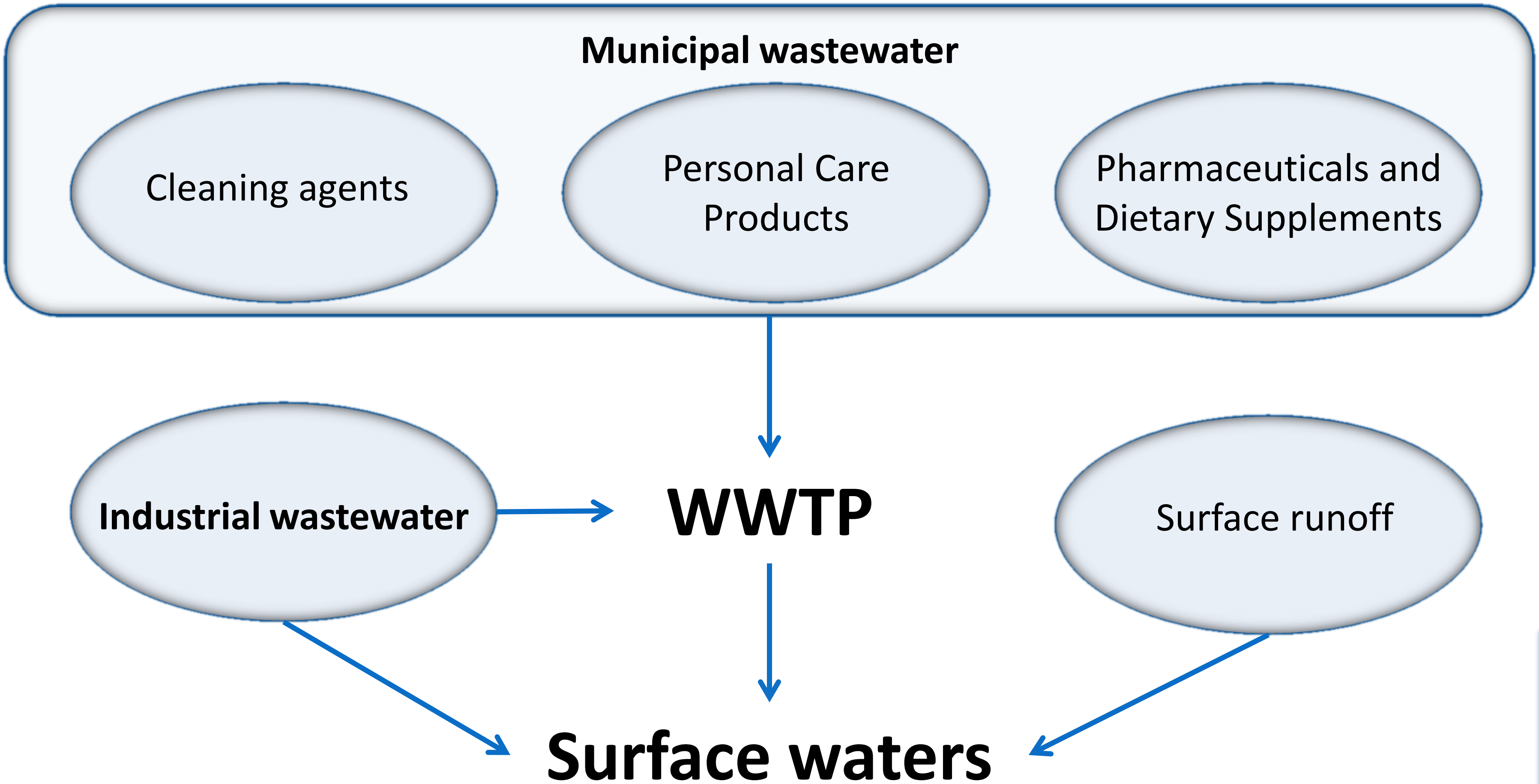
Silesian University of Technology

INTRODUCTON

Contaminants of Emerging Concern (CECs), including Pharmaceuticals and Personal Care Products (PPCPs) are in general:

- hardly or non-biodegradable compounds;
- biologically active;
- potential toxic against aquatic organisms;
- commonly identified in the environment, including the water environment.

Anthropogenic organic compounds in the water environment



OBJECTIVE

Comparison of removal degrees of organic micropollutants in water solutions during selected AOPs such as H_2O_2, O_3, UV and UV/TiO_2.

To determine the susceptibility of particular types of micropollutants to oxidation processes different groups of contaminants of emerging concern were tested i.e. **pharmaceuticals**, **dyes**, **UV blockers**, **pesticides**, **hormones** and **food additives**.

Table 1. Characteristic of the tested organic compounds.

Group	Name	Molecular formula	Molecular weight, g/mol	Solubility in water, mg/L	pK_a
Pharmaceuticals	Carbamazepine, CBZ	$C_{16}H_{12}N_2O$	236.30	17	2.30
	Benzocaine, BE	$C_9H_{11}NO_2$	165.19	1310	2.51
	Diclofenac sodium salt, DCF	$C_{14}H_{10}Cl_2NNaO_2$	318.13	50	4.15
	Ibuprofen sodium salt, IBU	$C_{13}H_{17}NaO_2$	228.26	100	4.91
Dyes	Acridine, ACR	$C_{13}H_9N$	179.22	38.4	5.6
UV blockers	Dioxybenzone, BZ8	$C_{14}H_{12}O_4$	244.24	Insoluble	6.99
Pesticides	Triallat, TRI	$C_{10}H_{16}Cl_3NOS$	304.66	4.1	-
	Triclosan, TCS	$C_{12}H_7Cl_3O_2$	289.54	0.1	7.9
	Oxadiazon, ODZ	$C_{15}H_{18}Cl_2N_2O_3$	345.22	0.7	-
Hormones	β-Estradiol, E2	$C_{18}H_{24}O_2$	272.38	3.6	10.33
	17α-Ethinylestradiol, EE2	$C_{20}H_{24}O_2$	296.40	11.3	10.33
	Mestranol, EEME	$C_{21}H_{26}O_2$	310.43	1.13	17.59
	Progesterone, P4	$C_{21}H_{30}O_2$	314.46	8.81	18.92
Food additives	Butylated Hydroxytoluene, BHT	$C_{15}H_{24}O$	220.35	0.6	12.23
Other	Caffeine, CAF	$C_8H_{10}N_4O_2$	194.19	21600	14.0

Tested Water Samples

Deionized water solutions with the addition of patterns of the tested organic micropollutants of the concentration of 500 μg/L constituted the subject of the study. The pH of the prepared water solutions was adjusted to 7.

The experiments for all tested compounds were carried out separately.

Advanced Oxidation Processes

Dose of H_2O_2: 3, 6, 9 and 12 mg/L.
Dose of O_3: 1, 3, 5 and 10 mg/L.
Contact time between the oxidizing reagents and the water solutions was 30 min.

Power of the UV lamp: 150 W.
Dose of TiO_2: 50 mg/L.
Irratiation time : 10, 30 and 60 min.

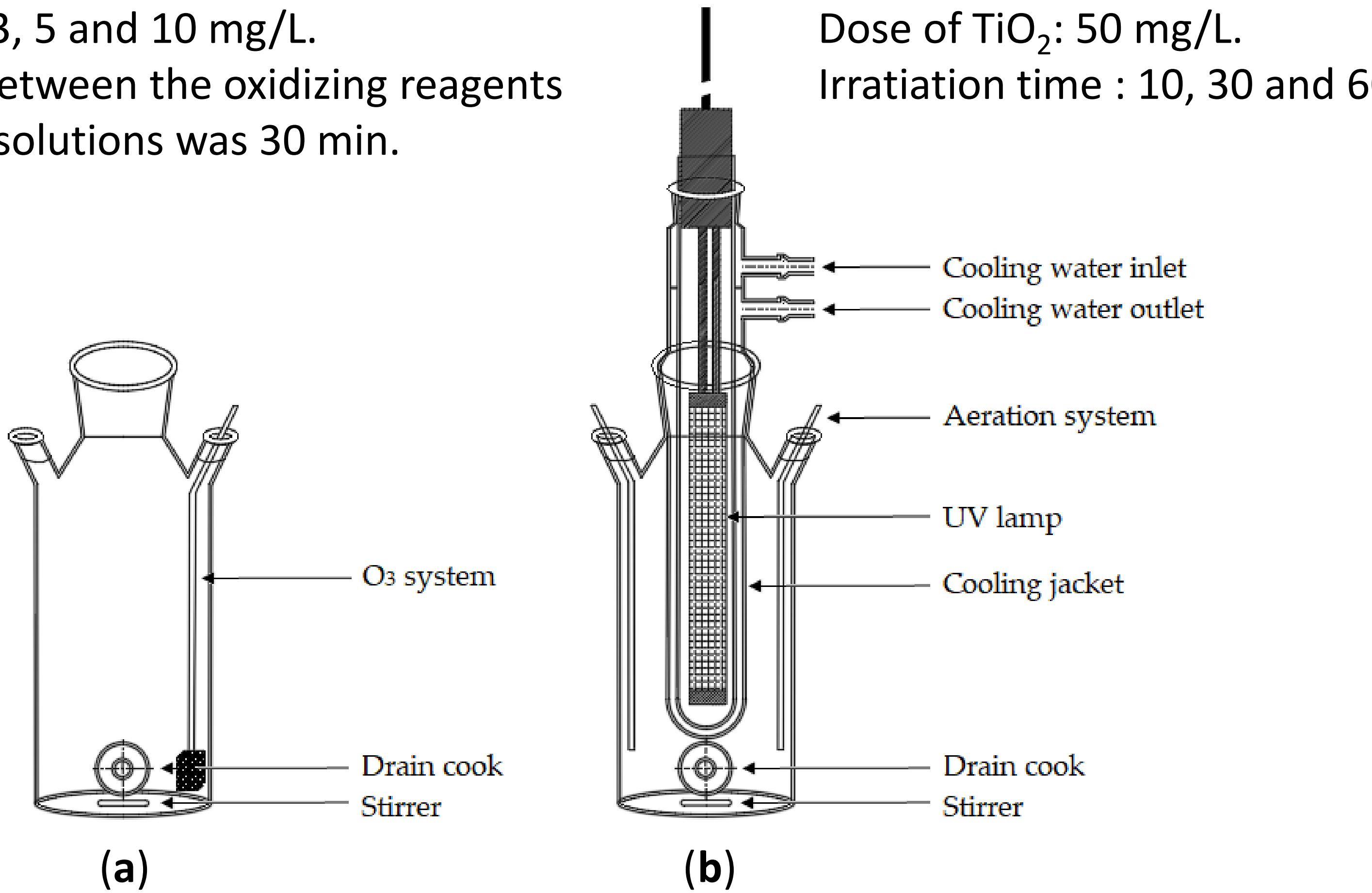


Figure 1. Reactor for the (**a**) H_2O_2, O_3 and (**b**) UV, UV/TiO_2 process

Analytical Procedure

The analytical procedure of tested compounds was performed by the use of the GC-MS chromatography with electron ionization preceded by Solid Phase Extraction (SPE).
The volume of analyzed water samples was equal to 20 mL.

Table 2. Solid Phase Extraction details for different compound groups.

Compound group	**Pharmaceuticals** **Food additive**	**Dyes** **UV blocker** **Pesticides** **Other**	**Hormones**
Cartridge type	Supelclean™ ENVI-8	Supelclean™ ENVI-18	Supelclean™ ENVI-18
Conditioning	5.0 mL of MeOH	5.0 mL of ACN 5.0 mL of MeOH	3 .0 mL of DCM 3.0 mL of ACN 3.0mL of MeOH
Washing		5.0 mL of deionized water	
Extract elution	3.0 mL of MeOH	1.5 mL of MeOH 1.5 mL of ACN	2.0 mL of DCM 1.5 mL of ACN 1.5 mL of MeOH

Toxicity Assestment

The Microtox® test was use to determine the toxic potential of the micropollutant water solutions before and after the oxidation processes. The bioassay is based on the measurement of the intensity of light emission by selected strains of luminescent bacteria *Aliivibrio fischeri*.

The test procedure assumes the estimation of the toxic effect of the tested sample comparative to a reference nontoxic sample (2% NaCl solution).

RESULTS

Degradation of Micropollutants in the H_2O_2 process

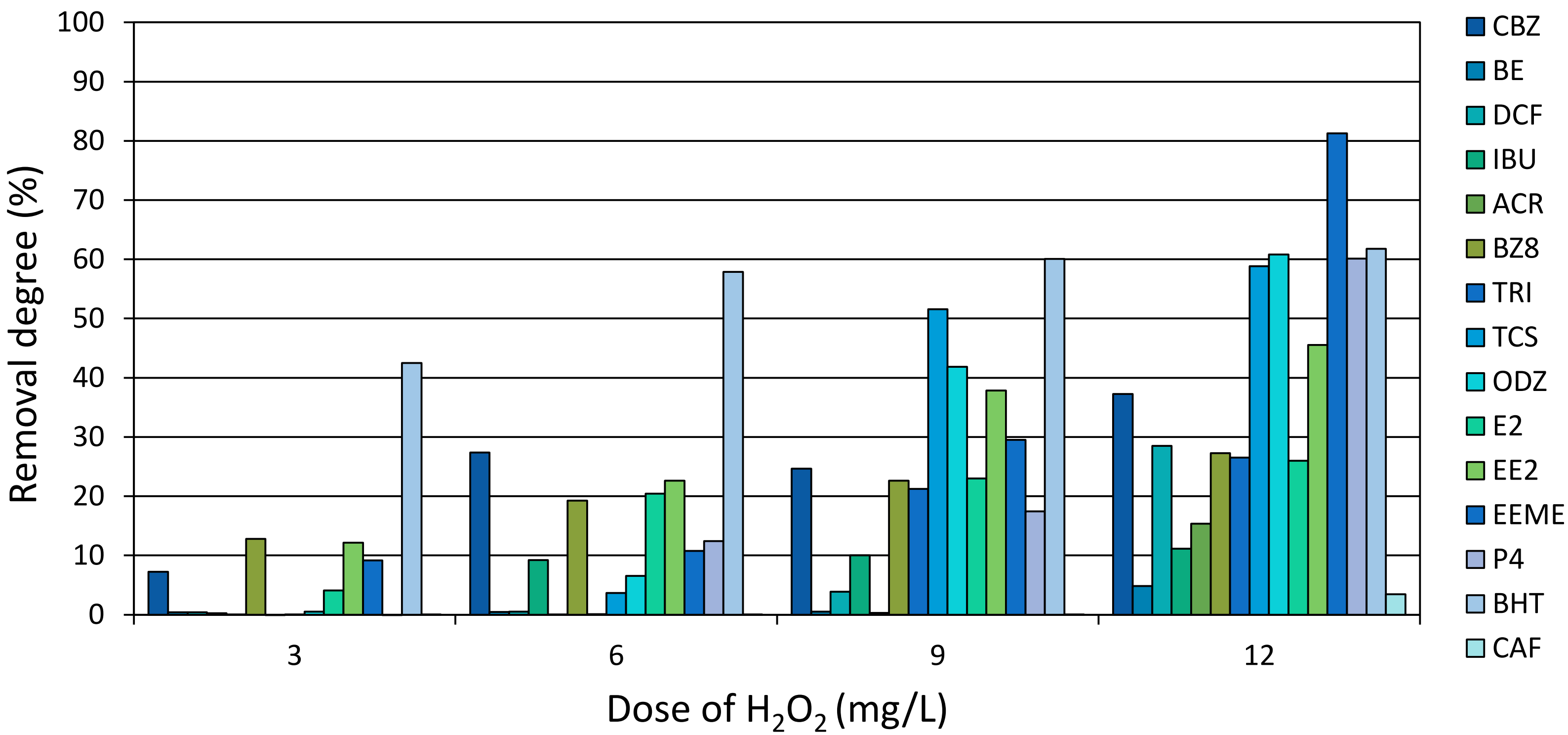


Figure 2. Influence of the H_2O_2 dose on the decomposition of micropollutants

RESULTS
Degradation of Micropollutants in the O_3 process

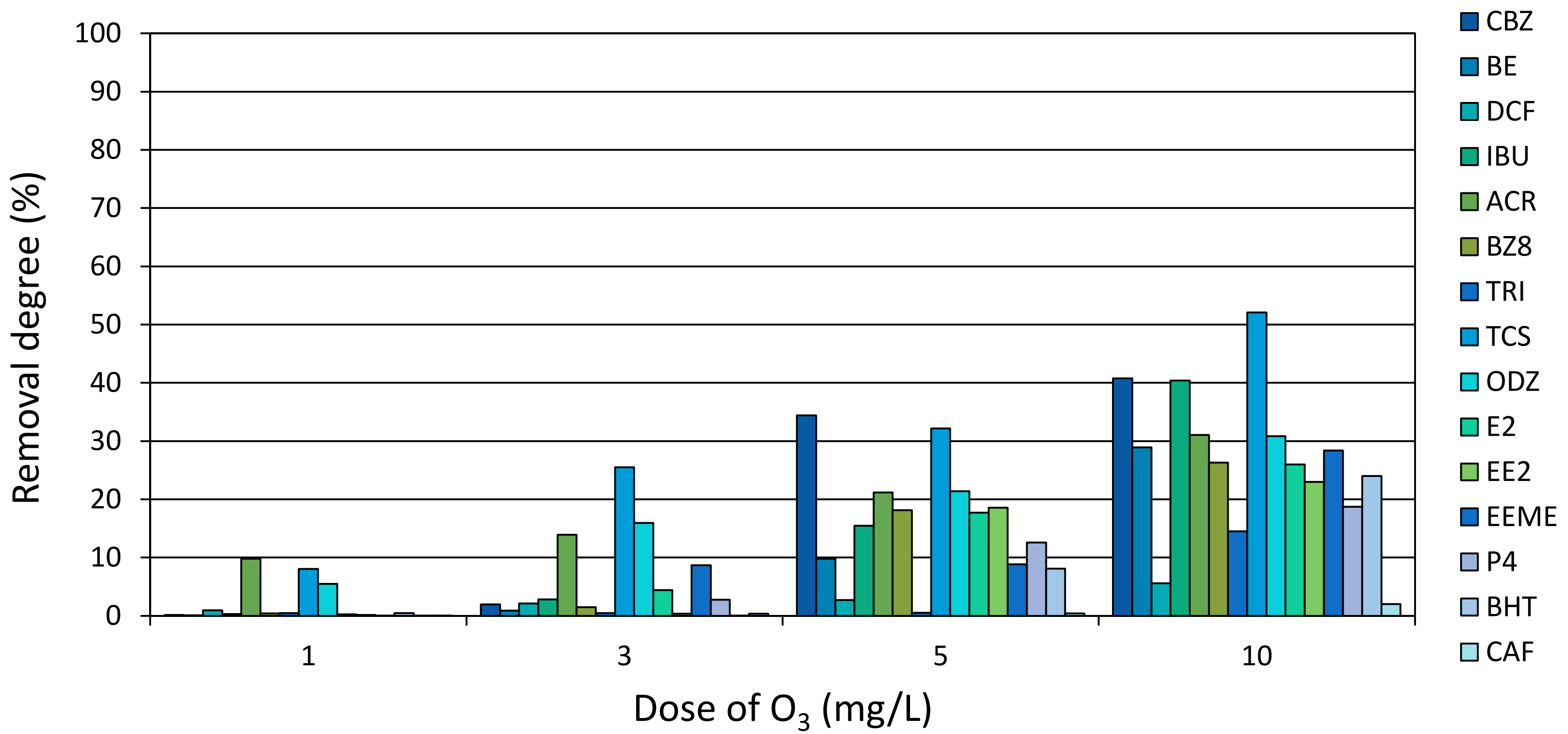


Figure 3. Influence of the O_3 dose on the decomposition of micropollutants

Silesian University of Technology

ECWS

Sponsored by: MDPI water

RESULTS

Degradation of Micropollutants in the UV process

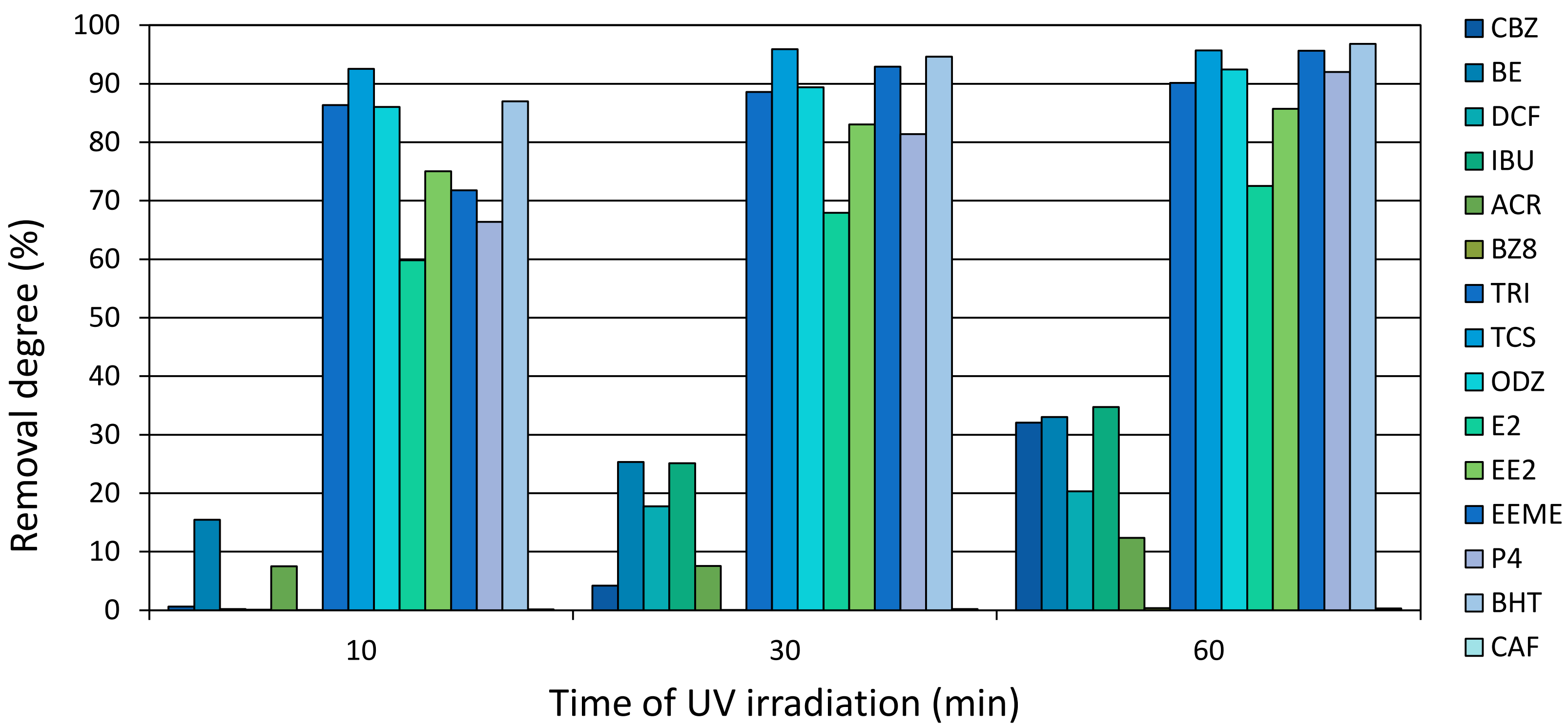
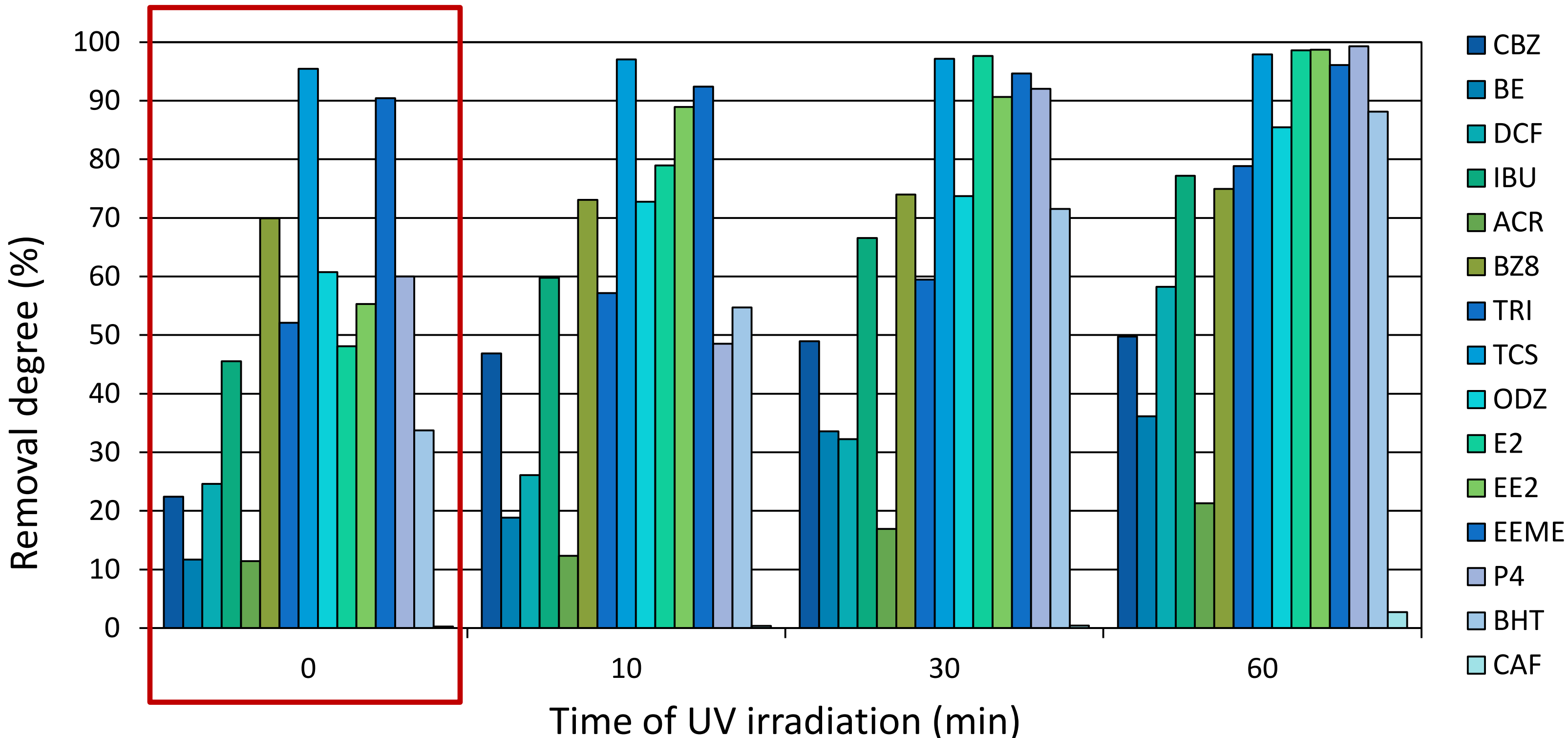


Figure 4. Influence of the UV irradiation time on the decomposition of micropollutants

RESULTS

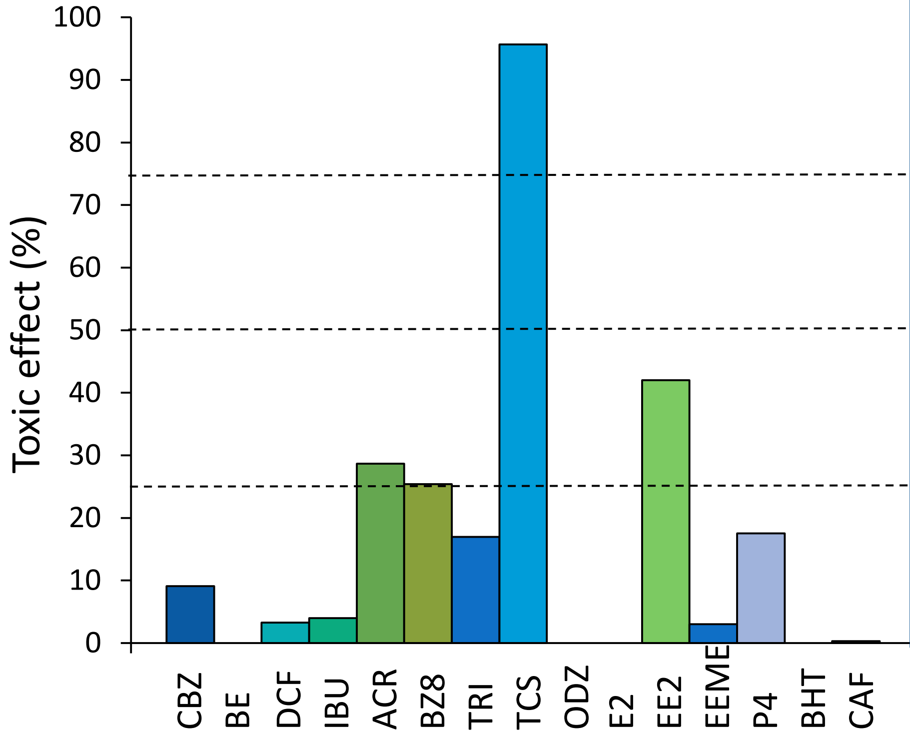
Degradation of Micropollutants in the UV/TiO_2 process



Adsorption of compounds on the TiO_2 surface

Figure 5. Influence of the UV irradiation time on the decomposition of micropollutants

RESULTS - Toxicological Assessment



Toxicity classification

	Effect (%)
Highly toxic	> 75,00
Toxic	50,01 – 75,00
Low toxic	25,00 – 50,00
Non toxic	< 25,00

Figure 6. Toxicity of micropollutant water solutions before the implementation of oxidation processes

RESULTS - Toxicological Assessment

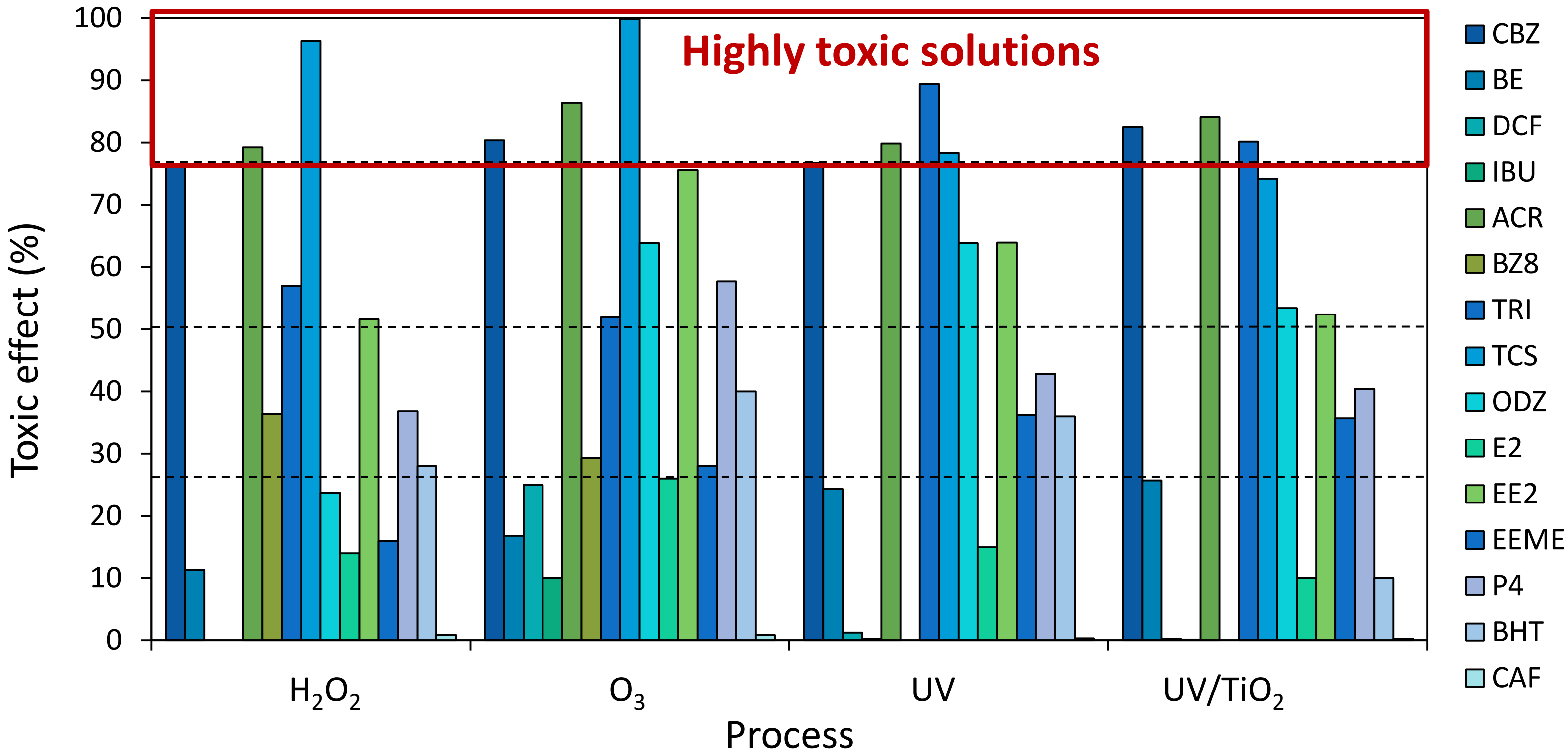


Figure 7. Change in toxicity o micropollutant water solution after selected oxidation processes

CONCLUSIONS

- UV-based oxidation processes are more effective for the micropollutant decomposition than the H_2O_2 and O_3 process.
- The highest removal rate of pharmaceutical compounds was observed during the UV/TiO_2 process. Only acridine was more effective oxidize by the O_3 process. The TiO_2 supported process allows also for a 96% removal of hormones.
- Pesticides and the food additive BHT were mostly effective oxidized by the UV process and their removal degrees exceeded 90%.
- Dioxybenzone was mainly reduced by the process of adsorption on the surface of the TiO_2 catalyst 75%.
- The lowest removal degree in all examined processes was observed in case of caffeine. The removal of this compound requires the implementation of different types of treatment processes such as membrane technologies.
- The toxicological analysis of post-processed water samples indicated the generation of several oxidation by-products with a high toxic potential.